

Inorganic Chemistry

**Principles of
Structure and
Reactivity**

Fourth Edition

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 HarperCollins College Publishers

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About the Cover

The crystal structure of *boggsite*, a recently discovered natural zeolite, is composed of sodium, calcium, aluminum, silicon, hydrogen, and oxygen. Its unique atomic structure of ten and twelve rings was determined by J. J. Pluth and J. V. Smith, geophysicists at the University of Chicago. Modeling tools used to construct the cover photograph are being developed in the Catalysis and Sorption Project of BIOSYM Technologies, Inc., San Diego, California. Structure of boggsite courtesy of Pluth, J. J.; Smith, J. V. *Am. Mineral.* 1990, 75, 501-507, and computer graphic by John M. Newsam, BIOSYM Technologies, Inc.

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Inorganic Chemistry: Principles of Structure and Reactivity, Fourth Edition

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This discovery was made in the 1850s, and it was the first ion exchange water-softening process utilized commonly. The ion exchangers used today in home softening units are closely related in structure and exchange properties, but are more stable for long-term use.

More recently, synthetic zeolites have made their appearance in a closely related, yet quite distinct, application. Not everyone, even in areas of quite hard water, has a water softener. In an effort to counter the negative effects of hard water, manufacturers early adopted the practice of adding “builders” to soaps and synthetic detergents. At first these were carbonates (“washing soda”) and borates (“borax”). More recently, these have been polyphosphates, $[\text{O}_3\text{PO}(\text{PO}_3)_n]^{m-}$ ($m = n + 3$), which complexed the hard water cations, that is, tied them up so that they did not interfere with the cleaning process. The synthesis of polyphosphates and the study of their chelating properties with Mg^{2+} , Ca^{2+} , and other cations, are other aspects of inorganic chemistry. However, phosphate is one of the three main ingredients of fertilizer,⁴ and too much phosphorus leads to the *eutrophication* of lakes and streams. In an effort to reduce the amount of phosphates used, manufacturers started using a synthetic zeolite in detergents in the form of microscopic powder to adsorb these unwanted cations. Today, this is the largest usage of zeolites on a tonnage basis.

Lest you be muttering, “So out with phosphate pollution, in with zeolite pollution!”, zeolites seem to be one of the few things we can add to the ecosystem without negative consequences. The very structures of zeolites make them thermodynamically unstable, and they degrade readily to more stable aluminosilicates that are naturally occurring clays. But that raises other interesting questions: If they are metastable, why do they form, rather than their more stable decomposition products? How can we synthesize them?

Another use of zeolites has been as “molecular sieves.” This very descriptive, if slightly misleading, name comes from a remarkable property of these zeolites: their ability to selectively adsorb molecules on the basis of their size. A mixture of gases may be separated according to their molecular weights (sizes) just as a coarse mixture may be separated by a mechanical sieve. Some chemistry labs now have “exhaust-less hoods” that selectively adsorb larger, noxious molecules, but are inert to smaller, ubiquitous molecules such as water, dinitrogen (N_2), and dioxygen (O_2). There are zeolites that have a special affinity for small molecules (like H_2O) but exclude larger molecules. They are thus excellent drying agents for various laboratory solvents.

Chemical Structure of Zeolites and Other Chemical Systems

Before we can understand how these molecular interactions can take place, we must understand the *structures* of zeolites. Important for at least a century, the use of structural information to understand chemistry is more important now than ever before. The determination of chemical structures is a combination of careful experimental technique and of abstract reasoning. Because we have seen pictures of “tinker-toy” molecules all our lives in TV commercials and company logos, it is almost impossible for us to realize that it has not been long in terms of human history since arguments were made that such structures could not be studied (or even could not *exist!*) because it was impossible to see atoms (*if* they existed). The crystallographer’s ability to take a crystal in hand and to determine the arrangement of invisible atoms (Fig. 1.1) is a

⁴ When you buy an ordinary “5-10-5” fertilizer, you are buying nitrogen (5%, expressed as N), phosphate (10%, expressed as P_2O_5), and potassium (5%, expressed as K_2O).

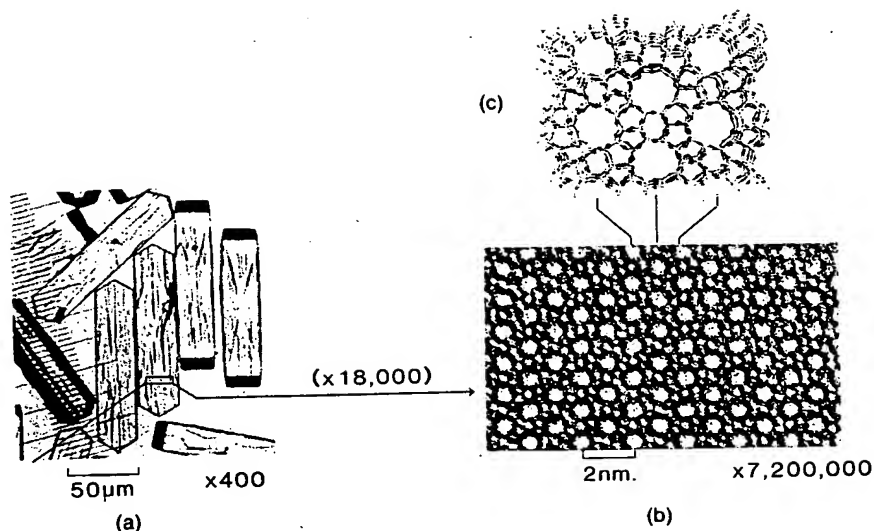


Fig. 1.1 The structure of the synthetic zeolite ZSM-5: (a) microscopic crystals; (b) an electron micrograph of the area marked in (a); (c) the crystal structure of ZSM-5 related to the electron micrograph. [Courtesy of J. M. Thomas, Royal Institute of Chemistry.]

triumph of abstract reasoning. The determination of the structures of molecules and extended structures is fundamental to the understanding of inorganic chemistry. It is not possible to think of modern inorganic chemistry in terms of simple equations such as Eq. 1.1 to 1.3: A three-dimensional view of the arrangement of atoms is necessary.

One of the unifying factors in the determination of chemical structures has been the use of symmetry and group theory. One has only to look at the structure of boggside to see that it is highly symmetrical, but symmetry is even more basic to chemistry than that. Symmetry aids the inorganic chemist in applying a variety of methods for the determination of structures. Symmetry is even more fundamental: The very universe seems to hinge upon concepts of symmetry.

The solid-state chemist and solid-state physicist have also developed other techniques for examining and manipulating solids and surfaces. Of particular interest recently is a technique known as *scanning tunneling microscopy* (STM) which allows us to see and even to move individual atoms.⁵ The atoms are imaged and moved by electrostatic means (Fig. 1.2).⁶ Although chemistry is portrayed, correctly, in terms of single atoms or groups of atoms, it is practiced in terms of moles (6×10^{23} atoms), millimoles (6×10^{20} atoms), or even nanomoles (6×10^{14} atoms), seldom less. But perhaps the horizon of atom-by-atom chemistry is not far away.

⁵ Some people object to the use of the verb "to see" in this context, correctly arguing that since the wavelength of visible light is much greater than the order of magnitude of molecules, the latter cannot be seen directly, but must be electronically imaged. True, but every year hundreds of millions of people "see" the Super Bowl on TV! What's the difference?

⁶ Eigler, D. M.; Schweizer, E. K. *Nature* 1990, 344, 524–526.

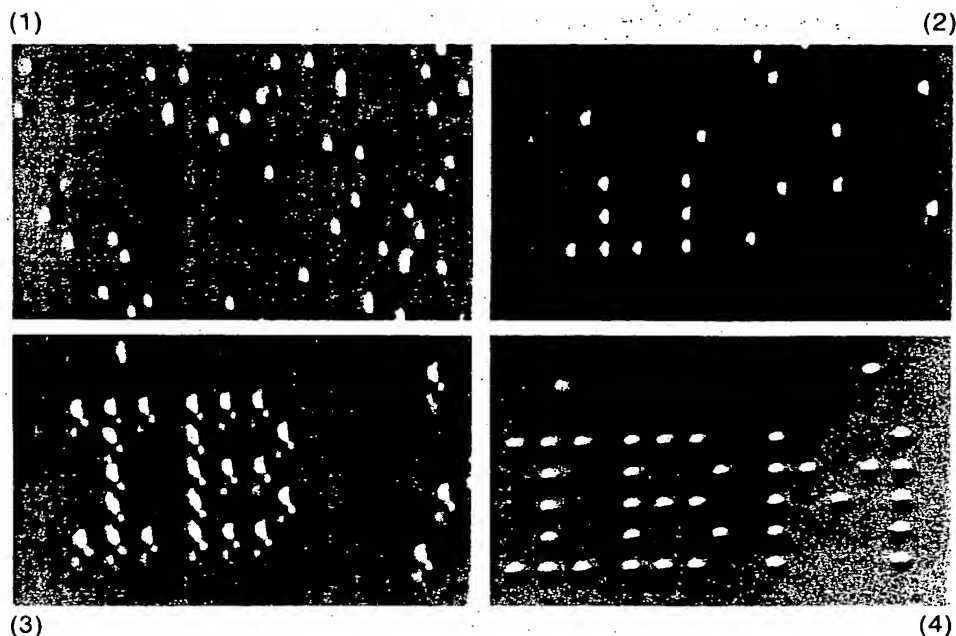
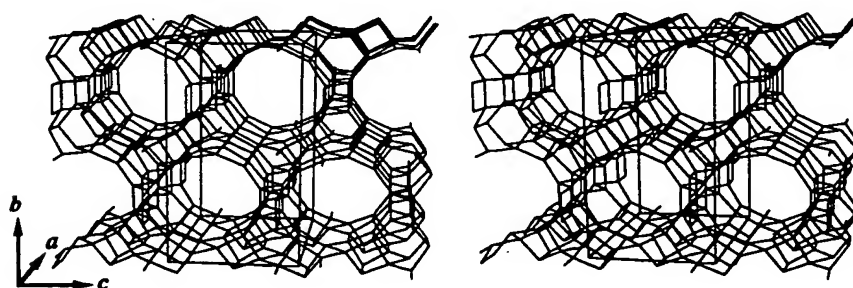


Fig. 1.2 Scanning tunneling micrographs of the movement of xenon atoms adsorbed on a nickel surface. The nickel atoms are not imaged. Each letter is 5 nm from top to bottom. [Courtesy of D. M. Eigler, IBM.]

Chemical Reactivity

Although it is not possible for the chemist to absolutely control the movement of individual atoms or molecules in zeolite structures, the nature of the structure itself results in channels that direct the molecular motions (Fig. 1.3). Furthermore, the sizes and shapes of the channels determine which molecules can form most readily, and which can leave readily. A molecule that cannot leave (Fig. 1.4) is apt to react further. This may have important consequences: A catalyst (ZSM-5) that is structurally related to boggsite is used in the alkylation of toluene by methanol to form *para*-xylene. The methanol can provide methyl groups to make all three (ortho, meta, and para)

Fig. 1.3 Stereoview of the structure of boggsite. Note the channels running in the *a* direction. For help in seeing stereoviews, see Appendix H. [From Pluth, J. J.; Smith, J. V. *Am. Mineral.* 1990, 75, 501–507. Reproduced with permission.]



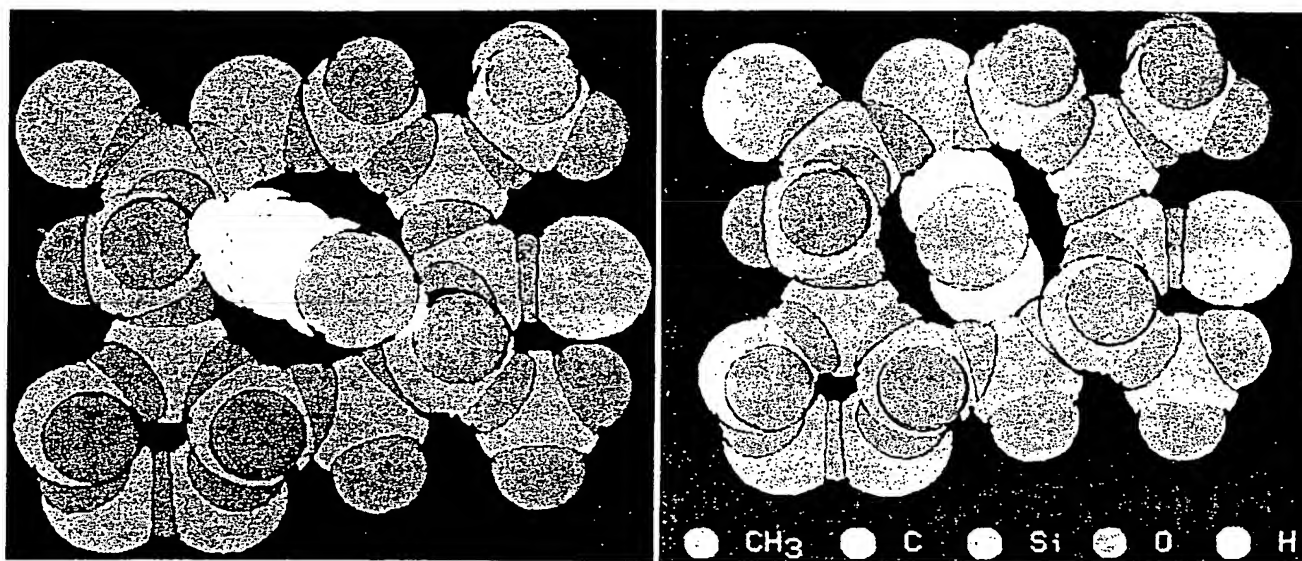


Fig. 1.4 *meta*-Xylene (left) and *para*-xylene (right) in a channel in the synthetic zeolite catalyst ZSM-5. [From Thomas, J. M. *Angew. Chem. Int. Ed. Engl.* 1988, 27, 1673–1691. Reproduced with permission.]

xylene isomers. The “linear” *para* isomer leaves readily (Fig. 1.5), but the angular *ortho* and *meta* isomers do not. They may react further, that is, rearrange, and if *para*-xylene forms, it may then leave.⁷

In a related process, ZSM-5 may be used to convert methanol into a high-octane gasoline. Petroleum-poor countries like New Zealand and South Africa are currently using this process to produce gasoline. If the production of *para*-xylene and gasoline sounds too much like “organic chemistry” for the introduction to an inorganic textbook, it must be pointed out that there is a large branch of chemistry,

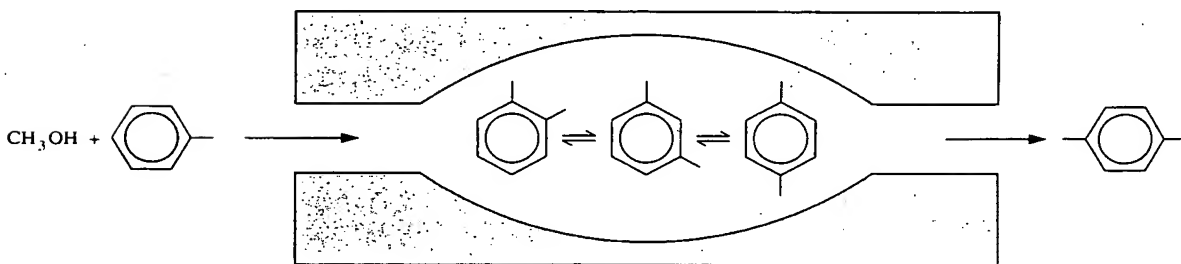
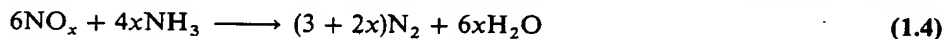


Fig. 1.5 Illustration of shape selectivity. [Csicsery, S. M. *Chem. Brit.* 1985, 21, 473–477. Reproduced with permission.]

⁷ So, in lieu of “chemical tweezers” (STM and related apparatus) we claim to effect particular stereochemical syntheses by using specially shaped zeolites. But it is stated that these specially shaped zeolites are *also* synthesized—without “chemical tweezers”. How? The answer is not as difficult as it may seem.

called "organometallic chemistry," that deals with an area intermediate between inorganic and organic chemistry and broadly overlapping both. Both organic and inorganic chemists work in organometallic chemistry, with the broad generalization often being that the products are "organic" and mostly of interest to the organic chemist, and the intermediates and catalysts are of more interest to the inorganic chemist.

Zeolites may be used in purely inorganic catalysis, however. One reaction that may be used to reduce air pollution from mixed nitrogen oxides, NO_x , in the industrial production of nitric acid is catalytic reduction by ammonia over zeolitic catalysts:



The seriously polluting nitrogen oxides are thus reduced to two harmless molecules. The strong bond energies of the dinitrogen molecule and the water molecule are the driving forces; the zeolitic catalyst, in the ideal case, provides the pathway without being changed in the process.

A related catalytic removal of NO from automobile exhaust may come about from the reaction:



using a Cu(I)/Cu(II) exchanged zeolite as a redox catalyst.⁸

To return to the problem of the general invisibility of atoms, how does the chemist follow the course of a reaction if the molecules cannot be imaged? One way is to use spectroscopy. Thus the conversion of methanol, first to dimethyl ether, then to the higher aliphatic and aromatic compounds found in gasoline, can be followed by nuclear magnetic resonance (NMR) spectroscopy (Fig. 1.6). As the reaction proceeds, the concentration of the methanol (as measured by the intensity of the NMR peak at $\delta 50$ ppm) steadily decreases. The first product, dimethyl ether ($\delta 60$ ppm), increases at first and then decreases as the aliphatic and aromatic products eventually predominate.

Conclusion

So why did we pick boggsite for the cover? Is it "the most important" inorganic compound known? Certainly not! It is currently known from only one locality and in the form of extremely small crystal fragments.⁹ It is unlikely that it occurs anywhere on earth in sufficient quantities to be commercially important. Yet its discovery adds to our knowledge of the structural possibilities of zeolites and the conditions under which they form. And if we know enough about the structure of a material, we can usually synthesize it if we try hard enough. The synthesis of zeolites has progressed, though it must be admitted that there is much yet to be understood in the process. Boggsite is enough like ZSM-5, yet different, that it has attracted considerable attention. There is currently a massive effort in the chemical industry to try to synthesize this very interesting material.¹⁰ It may become an important industrial catalyst. Then again, it may not—only time will answer *that* question.

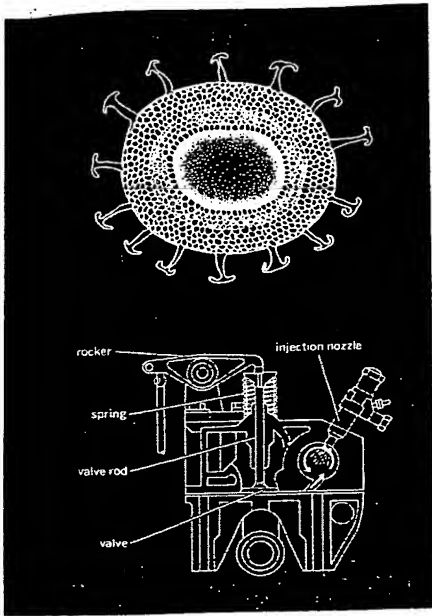
⁸ Iwamoto, M.; Yahiro, H.; Tanda, K.; Mizuno, N.; Mine, Y.; Kagawa, S. *J. Phys. Chem.* **1991**, *95*, 3727–3730.

⁹ Part of the difficulty in determining the crystal structure was in picking out a suitable crystal fragment from the matrix in which it was imbedded. Only one was found, $0.07 \times 0.08 \times 0.16$ mm in size. See Footnote 2.

¹⁰ Alper, J. *Science* **1990**, *248*, 1190–1191.

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by zinc See zincite.

RUBIDIUM

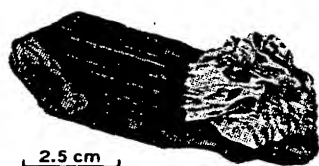
The image shows a standard periodic table of elements. The element Rubidium (Rb) is highlighted with a black box. An arrow points from the box to the element's position in the table, which is in the 5th period, 1st group. The table includes element symbols, atomic numbers, and names. The lanthanide and actinide series are shown at the bottom.

Periodic table of the chemical elements showing the position of rubidium.

split vertical photography spoofing

1.

SPODUMENE



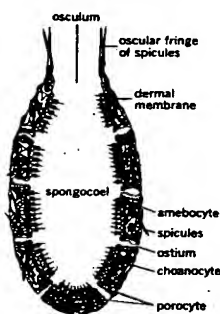
Spodumene crystal with
pegmatite, Doshen, Massachusetts.
(Specimen from Department of
Geology, Bryn Maur College)

SPONGILLIDAE



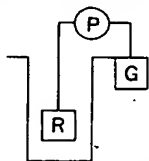
An encrusting spongiillid sponge
growing on a twig.

SPONGOCOEL



Morphology of asconoid
calcareous sponge—longitudinal
section. (After Hyman, 1940)

SPONTANEOUS-POTENTIAL WELL LOGGING



Basic pattern of spontaneous-
potential electric well logging;
P = potentiometer, G = grounded
electrode, and R = recording
electrode.

leading or lagging edge of the pulse so that it resembles two pulses and eventually a single pulse, which appears to be normal but which may be displaced in time by as much as 10,000 microseconds; this phenomenon is caused by shifting of the E_1 reflections from the ionosphere, and if the deformation is that of the leading edge and is not detected, it will cause serious errors in the reading of the navigational parameter. [MIN ENG] 1. Lamina of mica with a maximum thickness of 0.0012 inch (30 micrometers), split from blocks and thins. 2. One of a pair of horizontal level headings driven through a pillar, in pillar workings, in order to mine the pillar coal. **split vertical photography** [GRAPHICS] Photographs taken simultaneously by two cameras mounted at an angle from the vertical, one tilted to the left and one to the right, to obtain a small side lap.

SP logging See spontaneous-potential well logging.

Spodosol [GEOL] A soil order characterized by a spodic or plagic horizon overlying a fragipan.

spodumene [MINERAL] $\text{LiAlSi}_2\text{O}_6$ A white to yellowish-, purplish-, or emerald-green clinopyroxene mineral occurring in prismatic crystals; hardness is 6.5-7 on Mohs scale, and specific gravity 3.13-3.20; an ore of lithium. Also known as triphane.

spoil [MIN ENG] 1. The overburden or nonore material from a coal mine. 2. A stratum of coal and dirt mixed.

spoil bank [MIN ENG] 1. In surface mining, the accumulation of overburden. 2. The place where spoil is deposited. Also known as spoil heap.

spoil dam [MIN ENG] An earthen dike forming a depression, in which returns from a borehole can be collected and retained.

spoller [AERO ENG] A plate, series of plates, comb, tube, bar, or other device that projects into the airstream about a body to break up or spoil the smoothness of the flow, especially such a device that projects from the upper surface of an airfoil, giving an increased drag and a decreased lift. [ELECTROMAG] Rod grating mounted on a parabolic reflector to change the pencil-beam pattern of the reflector to a cosecant-squared pattern; rotating the reflector and grating 90° with respect to the feed antenna changes one pattern to the other.

spoil heap See spoil bank.

spoke [DES ENG] A bar or rod radiating from the center of a wheel.

spokeshave [ENG] A small tool for planing convex or concave surfaces.

spondylitis [MED] Inflammation of the vertebrae.

spondylolisthesis [MED] Forward displacement of a vertebra upon the one below as a result of a bilateral defect in the vertebral arch, or erosion of the articular surface of the posterior facets due to degenerative joint disease.

sponge [INV ZOO] The common name for members of the phylum Porifera.

sponge gold See cake of gold.

sponge grease [MATER] Fibrous, spongy, soda-base grease.

sponge iron [MET] Iron in porous or powder form made without fusion by heating iron ore in a reducing gas or with charcoal.

sponge metal [MET] Any porous metal made by decomposition or reduction of a compound without melting.

sponge rubber See rubber sponge.

spongework [GEOL] A pattern of small irregular interconnecting cavities on walls of limestone caves.

Spongiidae [INV ZOO] A family of sponges of the order Dictyoceratida; members are encrusting, massive, or branching in form and have small spherical flagellated chambers which characteristically join the exhalant canals by way of narrow channels.

Spongiillidae [INV ZOO] A family of fresh- and brackish water sponges in the order Haplosclerida which are chiefly gray, brown, or white in color, and encrusting, massive, or branching in form.

sponglin [BIOCHEM] A scleroprotein, occurring as the principal component of skeletal fibers in many sponges.

spongoblast [EMBRYO] A primordial cell arising from the ectoderm of the embryonic neural tube which differentiates to form the neuroglia, the ependymal cells, the neurolemma sheath cells, the satellite cells of ganglions, and Müller's fibers of the retina.

spongocyte [HISTOL] 1. A neuroglia cell. 2. A cell of adrenal cortex which has a spongy appearance due to solution of lipids during tissue preparation for microscopic examination.

Spongiomorphida [PALEON] A small, extinct Mesozoic or of fossil colonial Hydrozoa in which the skeleton is reticulum composed of perforate lamellae parallel to upper surface and of regularly spaced vertical elements in form of pillars.

Spongiomorphidae [PALEON] The single family of extinct hydrozoans comprising the order Spongiomorphida.

spongocoel [INV ZOO] The branching, internal cavity of a sponge, connected to the outside by way of the oscula.

spongolite [GEOL] A rock or sediment composed chiefly of the remains of sponges. Also known as spongolith.

spongolith See spongolite.

spongy mesophyll [BOT] A system of loosely and irregularly arranged parenchymal cells with numerous intercellular spaces found near the lower surface in well-differentiated broad leaves. Also known as spongy parenchyma.

spongy parenchyma See spongy mesophyll.

sponson mount [ORD] A gun mount positioned on the sponson of a tank or combat vehicle. Practically abandoned because of vulnerability and limited field of fire, although widely used in earlier tanks.

sponsor [COMMUN] The advertiser who pays part or all the cost of a television or radio program.

spontaneous [PHYS] Occurring without application of external agency, because of the inherent properties of object.

spontaneous abortion [MED] An unexpected, premature expulsion of the fetus.

spontaneous amputation [MED] 1. Congenital amputation. 2. Amputation not caused by external trauma or injury, as aninhum.

spontaneous fission [NUC PHYS] Nuclear fission in which particles or photons enter the nucleus from the outside.

spontaneous generation See abiogenesis.

spontaneous heating [CHEM] The slow reaction of matter with atmospheric oxygen at ambient temperatures; liberates heat, if undissipated, accumulates so that in the presence of combustible substances a fire will result.

spontaneous ignition [CHEM] Ignition which can occur when certain materials such as tung oil are stored in bulk resulting from the generation of heat, which cannot be read dissipated; often heat is generated by microbial action.

spontaneous magnetization [ELECTROMAG] Magnetization which a substance possesses in the absence of an applied magnetic field.

spontaneous mutation [GEN] A mutation that occurs naturally.

spontaneous nucleation [METEOROL] The nucleation of phase change of a substance without the benefit of a seeding nuclei within or otherwise in contact with the substance; examples of such systems are a pure vapor condensing to its pure liquid state, a pure liquid freezing to pure solid state, and a pure solution crystallizing to yield pure solute crystals.

spontaneous polarization [ELEC] Electric polarization that a substance possesses in the absence of an external electric field.

spontaneous-potential well logging [ENG] The recording of the natural electrochemical and electrokinetic potential between two electrodes, one above the other, lowered into drill hole; used to detect permeable beds and their boundaries. Also known as SP logging.

spontaneous process [THERMO] A thermodynamic process which takes place without the application of an external agency, because of the inherent properties of a system.

spontaneous symmetry breaking [PHYS] A situation in which the solution of a set of physical equations fails to exhibit a symmetry possessed by the equations themselves; example is a magnet, in which the underlying equations describing the metal do not distinguish any direction of space from any other, but the magnet certainly does, since it points in some definite direction.

spoofing [ELECTR] Deceiving or misleading the enemy in electronic operations, as by continuing transmission on

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Z

zein (pronounced zee-in). The characteristic protein of corn, from which it is extracted on a commercial scale. Its molecule contains the amide group CONH_2 . It has good nutritional value and thus is used in coatings for capsules and for dietetic and special food preparations. It also has some application in paper coatings and in the textile field, both as a sizing agent and as a fiber for blending with wool.

zeolite. Clays or clay-like structures (aluminosilicates) which have ion-exchange properties and exhibit the behavior of molecular sieves. They are crystalline compounds composed of tetrahedrons of silicon oxide in which aluminum atoms have replaced some of the silicon. The crystalline complex forms channels and cages of varying size which are capable of exerting an ionic selectivity or "sieving" effect when placed in salt solutions. Thus, zeolite ion-exchange units are extensively used in water conditioning to remove calcium and magnesium ions by replacing them with sodium ions. These units can be regenerated by treatment with sodium chloride solutions. Modified zeolites are now widely used in the petroleum refining industry as cracking catalysts, almost to the exclusion of older types. *See also* ion exchange; molecular sieve.

zero group. The gases comprising the right-hand column of the Periodic Table (or in older variations, the left-hand column). It is variously designated as the "inert gas," "rare gas," or "noble gas" group. The first three elements of this group do not enter into chemical combination. The zero group was so named at a time when all its members were thought to have zero valence; but it was

later found that the last three members (krypton, xenon, and radon) have limited compound-forming ability. The most reasonable name for this group is therefore the noble gas group. *See also* noble; inert.

Ziegler catalyst. A type of organometallic catalyst named after its discoverer, Karl Ziegler (b. 1898), a German chemist, Nobel Prize 1963 shared with Giulio Natta (b. 1903), an Italian chemist. There are many variations in composition, but in general these catalysts are made up of an alkyl metal (the metal being in Groups I, II, or III of the Periodic Table) plus a halide of a transition metal (Groups IV to VIII). An example would be triethylaluminum, $(\text{C}_2\text{H}_5)_3\text{Al}$, plus titanium dichloride (TiCl_2) dispersed in a hydrocarbon solvent. These catalysts are of the stereospecific type, permitting close control of the chemical structure of the polymers formed; their discovery was an invaluable aid to the plastics industry. *See also* stereospecific; polypropylene.

zinc. A element.

Symbol	Zn	Atomic Wt.	65.38
State	Solid	Valence	2
Group	IIB	Isotopes	5 stable
Atomic No.	30		

Zinc, m.p. 419°C (786°F), is widely distributed in the earth's crust, usually as a sulfide ore; large deposits are in British Columbia, Ontario, Quebec, Utah, Colorado, and Australia. The metal is obtained by pyrometallurgical and electrochemical techniques. The most notable chemical property of zinc is its pronounced electropositive nature; it is third among the common met-

ORGANIC POLYMER CHEMISTRY

AN INTRODUCTION TO THE ORGANIC CHEMISTRY
OF ADHESIVES, FIBRES, PAINTS, PLASTICS AND
RUBBERS

Second edition

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The bulked latex is then diluted to a solids content of about 15% and coagulated by the addition of acetic or formic acid. The coagulum is sheeted on rollers, washed and dried. Two types of drying process are used. In the first method, the sheets of rubber are dried in wood smoke at about 60°C for 4 days; the resultant brown product is known as *smoked sheet*. In the second method, the sheets are dried in air at about 40°C for 7 days; the product is *pale crepe*. Compared to smoked sheet, pale crepe is more expensive to produce (since the drying conditions are more critical and require better control) and is more prone to subsequent mould growth; however, it has the advantage of being light coloured.

About 10% of the latex produced is exported, as such, from the plantations. Commonly, field latex is centrifuged to give *concentrated latex* which has a solids content of about 60%. To preserve such latices over long periods of time, ammonia and other bactericides are added.

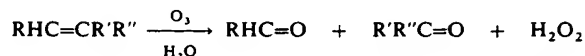
20.2.3 Structure

The principal component of the raw rubber of commerce is the single polymeric material known as *rubber hydrocarbon*. This is present to the extent of about 94%; the balance consists mainly of proteins, lipids, quebrachitol (monomethyl ether of hexahydroxycyclohexane) and inorganic salts. Pure rubber hydrocarbon may be obtained from raw rubber by fractional precipitation from dilute solutions. If, for example, methanol is added to a solution of raw rubber in toluene, the first fraction carries down most of the nitrogenous impurities and subsequent fractions consist of fairly pure rubber hydrocarbon; the other impurities remain in solution.

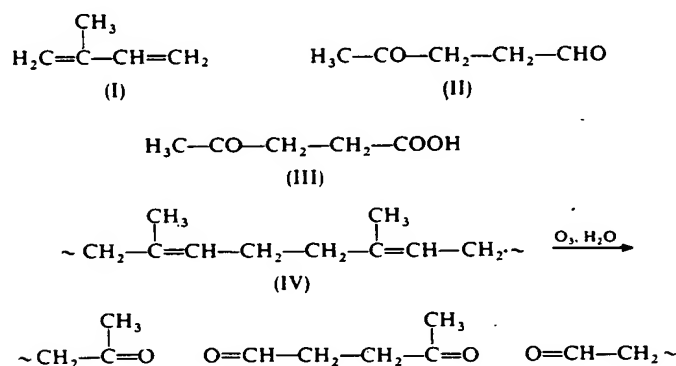
Although the minor constituents of rubber have some effect on the bulk properties, it is clearly the rubber hydrocarbon which determines the major features. Accordingly, the elucidation of the structure of rubber hydrocarbon has received the attention of many workers over the past 100 years or so. In 1826, Faraday established the empirical formula of rubber hydrocarbon as C_5H_8 and in 1860 Williams obtained isoprene (I) by dry distillation of rubber. In 1879, Bouchardat converted isoprene to a rubber-like material by treatment with hydrochloric acid and concluded that isoprene was the 'mother substance' of natural rubber. In 1888, Gladstone and Hibbert showed that rubber was unsaturated; under normal conditions, 2 atoms of bromine were added for each C_5H_8 unit.

Thus by the turn of the century it was generally accepted that rubber hydrocarbon could be represented as $(C_5H_8)_n$, but the way in which the units were joined was unknown. Important indications of the mode of linkage were obtained by Harries in 1904 during the course of extensive investigations into the action of ozone on olefins. It had been found that ozone reacts readily with unsaturated compounds to form products which, on hydrolysis, yield

aldehydes and/or ketones, depending on the structure of the starting material, e.g.



In practice, acids are also formed through oxidation of aldehyde by hydrogen peroxide. When Harries subjected rubber to ozonolysis, he obtained high yields of levulinic aldehyde (II) and levulinic acid (III). These results are readily explained if it is assumed that rubber hydrocarbon consists of isoprene units joined head-to-tail by 1,4-links (see also sections 1.4.2(a) and 1.6.3):



If the isoprene units were joined in some other way, ozonolysis would not yield levulinic aldehyde (and acid). It may be noted that Harries took his results to indicate that rubber hydrocarbon molecules were cyclic structures of low molecular weight which formed aggregates by means of ill-defined forces. This view was in accordance with the then current ideas concerning the nature of polymers. It was not until after 1920, when the concept of the macromolecule was introduced, that rubber hydrocarbon was accepted as consisting of linear polymers composed of isoprene units linked together by normal carbon-carbon bonds in a 1,4-, head-to-tail manner (see also section 1.3). Modern techniques of infrared and NMR spectroscopy have since verified the essential correctness of these conclusions; it has been shown that in rubber hydrocarbon at least 99% of the links between isoprene units are 1,4-bonds.

Examination of the structure of rubber hydrocarbon (IV) indicates the possibility of geometrical isomerism and Staudinger suggested that rubber contains mainly *cis*-1,4-bonds whilst gutta percha (section 20.2.7) has mainly *trans*-1,4-bonds. This assignment was made mainly on the basis of the lower density of rubber; it was well known that for simple molecules the *cis*-isomer generally has a lower density than the *trans*-isomer and the same relationship

was assumed to apply to polymeric materials. That rubber and gutta percha are respectively *cis*- and *trans*-geometrical isomers has subsequently been confirmed by X-ray analysis. It will be appreciated, of course, that ozonolysis of the two materials leads to identical products.

The molecular weight of rubber hydrocarbon is peculiarly difficult to measure and the results of various workers are not always in agreement. It is certain that the range of molecular weights present in the original latex is wide and thus the molecular weight distribution of a test sample is very dependent on the method of isolation. Furthermore, rubber hydrocarbon is rapidly degraded by oxygen and even on standing *in vacuo* in the dark some cross-linking appears to occur. The previous history of a sample is therefore likely to have substantial effects on molecular weight. In one investigation, in which pains were taken to eliminate degradation, an average molecular weight (M_w) of 1.3×10^6 was obtained [1].

Thus by the means outlined above, it has been established that natural rubber is essentially *cis*-1,4-polyisoprene. The final proof in this long endeavour may be considered to have been given in 1954 when the stereospecific polymerization of isoprene was achieved and 'synthetic natural rubber' was obtained (see section 20.3).

20.2.4 Vulcanization

As indicated in section 20.2.1, the term 'vulcanization' originally referred to the treatment of natural rubber with sulphur whereby the plasticity of the rubber was reduced whilst the elasticity was increased. The term now also includes other reagents which have similar effects, although sulphur has remained by far the most important vulcanizing agent. Further, the term now encompasses other elastomers besides natural rubber. From a chemical point of view, vulcanization is principally a process of cross-linking whereby the discrete linear rubber chains are converted into a three-dimensional network. In this way, the chains are prevented from slipping past one another when the sample is stressed and they return to their original positions when the stress is removed.

Technologically, the most important methods of vulcanizing natural rubber are by the use of accelerated sulphur systems and organic peroxides and only these methods are considered in this section.

(a) Accelerated sulphur vulcanization

The interaction between diene rubbers and sulphur is exceedingly complex and has been the subject of extensive investigation. In this book it is possible to give only an extremely brief account of the main conclusions of this work; more detailed reviews may be found elsewhere [2-5].